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[54] Title of Invention:　　Fluidized Bed Catalyst for the Production of Acrylonitrile from Propylene by Ammoxidation

[57] [Abstract]

This invention concerns a fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation, which includes a silicon dioxide support and a combination whose chemical formula, in terms of atomic ratios, is $A_aB_bC_cGe_dMn_eW_f Fe_gBi_hMo_iO_x$, in which formula A is selected as at least two elements from among Li, Na, K, Rb or Cs; B is selected as at least one element from among Co, Ni, Cr, Ca, Mg, La, Ce or V; C is selected as at least one element from among B, P or As. The catalyst of this invention is particularly suitable for use under conditions of lower reaction temperatures, higher reaction pressure and high propylene load; furthermore it maintains a high acrylonitrile yield-per-pass and a high propylene conversion rate and can be applied in industrial production.

1. A fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation which includes a silicon dioxide support and a combination whose chemical formula, in terms of atomic ratios, is as follows:

$$A_a B_b C_c Ge_d Mn_e W_f\, Fe_g Bi_h Mo_i O_x,$$

in which formula A is selected as at least two elements from among Li, Na, K, Rb or Cs;

B is selected as at least one element from among Co, Ni, Cr, Ca, Mg, La, Ce or V;

C is selected as at least one element from among B, P or As;

a assumes a value within the range of $0.01 \sim 1.5$;

b assumes a value within the range of $0.1 \sim 12.0$;

c assumes a value within the range of $0.1 \sim 0.6$;

d assumes a value within the range of $0.01 \sim 2.0$;

e assumes a value within the range of $0.01 \sim 2.5$;

f assumes a value within the range of $0.05 \sim 1.5$;

g assumes a value within the range of $0.1 \sim 4.0$;

h assumes a value within the range of $0.2 \sim 2.5$;

i assumes a value within the range of $12.0 \sim 14.5$;

x is the total number of oxygen atoms required by the chemical valence of individual elements within the catalyst

wherein the catalyst support is selected from silicon dioxide whose amount in terms of weight % is $30 \sim 70\%$.

2. The fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation described in item 1 of the Scope of Patent Claims characterized in that a assumes a value within the range of $0.01 \sim 0.7$.

3. The fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation described in item 1 of the Scope of Patent Claims characterized in that c assumes a value within the range of $0.1 \sim 0.45$.

4. The fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation described in item 1 of the Scope of Patent Claims characterized in that d assumes a value within the range of $0.01 \sim 1.0$.

5. The fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation described in item 1 of the Scope of Patent Claims characterized in that e assumes a value within the range of $0.2 \sim 1.5$.

6. The fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation described in item 1 of the Scope of Patent Claims characterized in that f assumes a value within the range of $0.1 \sim 1.0$.

Fluidized Bed Catalyst for the Production of Acrylonitrile from Propylene by Ammoxidation

This invention concerns a fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation.

Acrylonitrile is an important raw material in organic chemical industry. It is produced by ammoxidation of propylene. Through continuous research, a number of improvements have been made to obtain a high-activity and high-selectivity catalyst. These improvements mostly concern the catalyst's active composition and attach particular importance to proportions of the catalyst's active ingredients in increasing the activity and selectivity of the catalyst and hence in creasing the per-pass yield of acrylonitrile as well as production load.

Over the 30 years that synthesis of acrylonitrile by ammoxidation has been developing, factory production capacities have come close to matching the market demand. Lately, the primary trend in acrylonitrile production has been the renovation of existing plants rather than building new ones to reduce the waste of raw materials and increase production capacities. Through the renovation of existing plants, switching to high-efficiency catalysts and eliminating "bottlenecks" in the production process, the acrylonitrile production capacity can be increased by 50 ~ 80%, while required investments make up only 20~30% of those for new construction, thus yielding an enormous economic effect.

Plant renovation may run into two problems: 1 - the reaction pressure in the fluidized bed reactor will have to be increased; 2 – the amount of catalyst to be loaded cannot be too big. Therefore the replacement catalyst must have a relatively high propylene load and be capable of withstanding a high reaction pressure.

Reaction pressure in a fluidized bed reactor is determined by the dropping resistance of a number of heat exchangers, columns and pipes from the reactor outlet to the absorption tower. Since a growing production capacity will inevitably lead to an increasing amount of material at the reactor outlet, the above-mentioned drop of resistance will grow. In addition, the heat transfer surface of exchangers is insufficient and heat exchange equipment must be added, which further increases the resistance drop. For environmental reasons, it is prohibited to release the reaction exhaust gas at the top of the absorption tower directly into the atmosphere; instead, it is incinerated in a furnace. Thus without resorting to induced draft fan, the pressure at the top of the absorption tower will have to be raised. For the various reasons mentioned above, currently the operational pressure of reactors is 1.5 to 2 times greater than the design value, as high as 0.08 MPa or more.

The second issue mentioned above is the catalyst's load, i.e. WWH. It is defined as the number of tons that can be processed per hour per 1 ton of catalyst. Due to the reactor's increased inlet amount, the catalyst charging capacity must be increased

accordingly while the catalyst's load stays the same. However, in the original fluidized bed reactor, the cooling water system's height is inadequate, therefore the fluidization height of catalyst may exceed the height of the cooling water pipes. Furthermore, because of the reactor's increased inlet amount, the linear speed of operation displays a marked increase. The combined impact of these two changes may raise the temperature of the reactor's dilute phase, causing the formation of an increased amount of carbon dioxide and a drop in acrylonitrile selectivity. Therefore, all of the above-mentioned problems can be avoided with a comparatively high catalyst WWH. Moreover, effective reduction of the reaction temperature can both reduce energy dissipation and improve the conditions of reaction, thus achieving the goal of increased acrylonitrile yield.

Theoretically, raising the catalyst's WWH must raise activation energy of adsorption for propylene, but so far there have been no reports of certain elements within the catalyst being capable of increasing the activation energy of adsorption for propylene. In the source CN1021638C, a catalyst of the following composition has been suggested:

$$A_aB_bC_cNi_4Co_eNa_fFe_gBi_bM_iMo_jO_x.$$

In the formula A is potassium, rubidium, cesium, samarium, thallium; B is manganese, magnesium, strontium, calcium, beryllium, lanthanum, rare earth elements; C is phosphorus, arsenic, boron, antimony, chromium; M is tungsten, vanadium.

With the above-mentioned catalyst, a fairly high yield-per-pass of acrylonitrile can be achieved., but the catalyst's propylene load is pretty low, and at comparatively high reaction pressure, there is a significant drop in acrylonitrile yield-per-pass. Further research demonstrates that in the above-mentioned catalyst, components B and M are related to the catalyst's load and performance under high pressure. Certain elements within component B, even though they contribute to high acrylonitrile yield-per-pass, adversely affect the growth of catalyst's load and performance under high reaction pressure, so they are disadvantageous for use in operations under conditions of high pressure and high load. Furthermore, in CN1021638C, the i and j sum total in the above-mentioned catalyst is specified as 12, i.e., is a constant. In this invention, this stipulation is eliminated, since otherwise whenever the M component is increased the molybdenum component is diminished, which affects the acrylonitrile yield-per-pass.

In the documents US5688739 and US5770757 a germanium-containing ammoxidation catalyst was introduced that enables a high acrylonitrile yield. In this document, a system of molybdenum, bismuth, and germanium was used, with an optional alkali metal among the elements, however, in the Practical Examples, no example of including sodium was disclosed. Moreover, the only reaction condition disclosed in this document was that the reaction pressure was constant, but there was no specific data from a study under conditions of high pressure and high load.

The goal of this invention is to resolve the issues that were not addressed by the catalyst from the above-mentioned documents, suitability for high reaction pressure, high operation load and somewhat lower reaction temperatures, by offering a new fluidized bed catalyst for the production of acrylonitrile by propylene ammoxidation. This catalyst can be suitable for operation under conditions of higher reaction pressure, higher load, somewhat lower reaction temperature, and lower air/propylene ratio while retaining a high acrylonitrile yield-per-pass and a high propylene conversion rate.

The goal of this invention will be achieved by the following technological scheme: A fluidized bed catalyst for the production of acrylonitrile from propylene by ammoxidation which includes a silicon dioxide support and a combination whose chemical formula in terms of atomic ratios, is as follows:

$$A_a B_b C_c Ge_d Mn_e W_f Fe_g Bi_h Mo_i O_x,$$

in which formula A is selected as at least two elements from among Li, Na, K, Rb or Cs;

B is selected as at least one element from among Co, Ni, Cr, Ca, Mg, La, Ce or V;

C is selected as at least one element from among B, P or As;

a assumes a value within the range of $0.01 \sim 1.5$;

b assumes a value within the range of $0.1 \sim 12.0$;

c assumes a value within the range of $0.1 \sim 0.6$;

d assumes a value within the range of $0.01 \sim 2.0$;

e assumes a value within the range of $0.01 \sim 2.5$;

f assumes a value within the range of $0.05 \sim 1.5$;

g assumes a value within the range of $0.1 \sim 4.0$;

h assumes a value within the range of $0.2 \sim 2.5$;

i assumes a value within the range of $12.0 \sim 14.5$;

x is the total number of oxygen atoms required by the chemical valence of individual elements within the catalyst;

wherein the catalyst support is selected from silicon dioxide whose amount in terms of weight % is $30 \sim 70\%$.

In the above-mentioned technological scheme, the preferred range of values for a is $0.01 \sim 0.7$, the preferred range of values for c is $0.1 \sim 0.45$, the preferred range of values for d is $0.01 \sim 1.0$, the preferred range of values for e is $0.2 \sim 1.5$, the preferred range of values for f is $0.1 \sim 1.0$.

No special requirements are imposed on the method of manufacturing the catalyst of this invention; it can be done by the usual methods. First, a solution of the various catalyst components is prepared, and then it is mixed with the support into slurry and molded into microspheres by spray drying and finally calcined to prepare the catalyst. The slurry is best prepared by the method of CN 1005248C.

The raw materials for the catalyst of this invention are as follows.

For the molybdenum component of the catalyst – molybdenum oxide or ammonium molybdate.

For the phosphorus, arsenic and boron it is best to use corresponding acids or their ammonium salts; for tungsten ammonium tungstate or tungsten oxide can be used; for vanadium - ammonium metavanadate; for germanium – its oxide, for chromium – chromium trioxide, chromim nitrate or a mix of the two; for the other components their

nitrates or oxides can be used or they can be decomposed into oxide salts, but it is best to use water-soluble nitrates.

Raw materials that can be used for the silicon dioxide support include silicasol, silica gel or a mixture of both. When silicasol is used its quality must meet the requirements of CN 1005248C.

Once the slurry is prepared, it is then heated and condensed to a solid content of 47 ~ 55% and subsequently spray dried. The spray drying units used can be those of pressure type, two-fluid type or centrifugal turntable type, but the centrifugal type is preferred because it can ensure a good particle size distribution of the manufactured catalyst.

The catalyst calcination can be performed in two stages: the decomposition of the salts of various elements in the catalyst and high-temperature calcination. The best temperature at the decomposition stage is 200 ~ 300°C, its duration – 0.5~ 2 hrs. The calcination temperature range is 500 ~ 800°C, while 550 ~ 700° is the best; the duration of calcination can be from 20 minutes to 2 hours. The above-mentioned decomposition and calcination are performed in two separate calciners, but they also can be performed in two zones of a single calciner, or the decomposition and calcination can be performed simultaneously and continuously in a rotary calciner. An appropriate quantity of air must be blown through in the processes of decomposition and calcination, to prevent excessive reduction of the catalyst.

The standards to be met by propylene, ammonia, and molecular oxygen required for the production of acrylonitrile using the catalyst of this invention are the same as for other ammoxidation catalysts. Even though the low molecular saturated hydrocarbon content of the original propylene has no bearing on the reaction, but from the economic standpoint, the best content would be more than 85% (mol). As ammonia, the fertilizer grade liquid ammonia can be used. From the technological standpoint pure oxygen, enriched oxygen or air can be used as the required molecular oxygen, but air is the best due to economic and safety considerations.

The molar ratio of ammonia and propylene entering the fluidized bed reactor is 0.8 ~ 1.5, but 1.0 ~ 1.3 is the best. The molar ratio of air and propylene is 8 ~ 10.5 but 9.0 ~ 9.8 is the best. When, for reasons related to certain operations, a higher air ratio must be used it can be raised to 11 without any significant impact on the reaction. However, for safety reasons, the excessive oxygen within reaction gases must not exceed 7% (by volume), and it is best for it not to exceed 4%.

When the catalyst of this invention is used in a fluidized bed reactor, the reaction temperature is 420 ~ 470°C, while 425 ~ 450°C is the best. The catalyst of this invention is a catalyst suitable for a low reaction temperature, high pressure and high load, therefore reaction pressure in the production equipment can be higher than 0.08 MPa, for example 0.08 ~ 0.15 MPa. Should the reaction pressure be lower than 0.08 MPa, this will not have any adverse impact, while the acrylonitrile yield –per-pass can be further increased.

The propylene load (WWH) of the catalyst of this invention is 0.06 ~ 0.15 hr^{-1}, while the best is 0.07 ~ 0.10 hr^{-1}. When the load is too low this does not only mean a waste of catalyst but also can increase the amount of carbon dioxide produced and reduce the

selectivity, which is why it is undesirable. An excessively high load is practically pointless, because when the amount of catalyst is too small, the heat transfer area of the cooling water pipes in the catalyst layer may be too small to remove the reaction heat, thus producing a situation where the reaction temperature cannot be controlled.

In the recovery and purification process of the acrylonitrile produced with the catalyst of this invention, existing production processes can be applied without any modifications. That is, unreacted ammonia is removed along with the effluent gases from the fluidized bed reactor via neutralization tower, and then all of the organic products are absorbed by low temperature water. The absorption liquid undergoes extractive distillation, and an acrylonitrile product of high purity is obtained upon the removal of hydrocyanic acid and dehydration.

This invention reveals that due to the addition of germanium and tungsten to the molybdenum, bismuth and iron catalyst system, this catalyst system acquired a capability to operate under conditions of higher reaction pressure (0.14 MPa) and higher load (WWH is 0.085 hr^{-1}). It also reveals that due to the addition of a manganese component to this catalyst system, it has a higher catalytic activity and selectivity under reaction temperature of 430°C. Moreover, by appropriately adding other active components and non-metal elements B, P or/and As, even better results are achieved: this catalyst operates under conditions of a reaction temperature of 430°C, a higher pressure of 0.14 MPa, a higher load of 0.085 hr^{-1}, and a lower air to propylene ratio of 9.5:1 (mole), and the acrylonitrile yield-per-pass can become as high as 80.3%, while the ammonia conversion rate may reach 98%.

The activity of the catalyst of this invention was evaluated in a fluidized bed reactor with an internal diameter of 38 mm. The catalyst charge was 400 g, the reaction temperature was 430°C, the reaction pressure – 0.14 MPa, and the raw material's composition ratio (moles) was propylene : ammonia : air = 1 : 1.2 : 9.5; the catalyst's propylene load (WWH) was 0.085 hr^{-1}.

In this invention the definitions of propylene conversion rate, acrylonitrile selectivity and yield-per-pass are as follows:

$$\text{Propylene conversion rate (\%)} = \frac{\text{Reacted propylene mole number}}{\text{Fed propylene mole number}} \times 100$$

$$\text{Acrylonitrile selectivity (\%)} = \frac{\text{Produced acrylonitrile mole number}}{\text{Reacted propylene mole number}} \times 100$$

$$\text{Acrylonitrile yield-per-pass (\%)} = \frac{\text{Produced acrylonitrile mole number}}{\text{Fed propylene mole number}} \times 100$$

$$\text{Ammonia conversion rate (\%)} = \frac{\text{Fed ammonia mole number} - \text{unreacted ammonia mole number}}{\text{Fed ammonia mole number}} \times 100$$

Below we will further explain this invention with Practical Examples.

[Practical Example 1]

To 2.16 g of cesium nitrate mixed with 1.64 g of potassium nitrate was added 30 g of water and the mixture was heated to dissolving.to obtain substance (A). 7.02 g of germanium dioxide, 11.48 g ammonium tungstate, and 421.8 g of ammonium molybdate were dissolved in 350 g of hot water at 60 ~ 90°C. to obtain substance (B). 10.8 g of chromium trioxide was dissolved in 15 g of water to obtain substance (C). 67.2 g of bismuth nitrate, 17.47 g of manganese nitrate, 282 g of nickel nitrate, 48.4 g of cerous nitrate, 102 g of magnesium nitrate and 168 g of ferric nitrate were mixed together, 190 g of water was added thereto and once the mixture was heated to dissolving it became substance (D). By weighing 4.12 g of phosphoric acid solution, substance (E) was made.

Substance (A) was mixed with 1280 g of silicasol with a weight concentration of 40%, and while stirring the mixture, to it were added substances (B), (C), (D) and (E) one by one, and after complete stirring, slurry was obtained. The produced slurry was formed into microspheric particles by a commonly known method in a spray drier. Finally, it was calcined for 1.5 hrs at 590°C in a rotary calciner with an inner diameter of 89 mm and a length of 1700 mm (Φ 89 x 1700 mm), and the composition obtained was

50% $K_{0.1}Cs_{0.07}P_{0.020}Ni_{5.6}Cr_{0.35}Ce_{0.35}Mg_{1.2}Ge_{0.05}Mn_{0.2}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$ + 50% SiO_2.

[Practical Examples 2 ~ 8 and Comparative Examples 1 ~ 4]

By basically the same method as in Practical Example 1 were prepared catalysts whose compositions differed as indicated in Tables below. Then acrylonitrile was produced by propylene ammoxidation with the prepared catalysts under reaction conditions indicated below, and the results are shown in Table 1.

The reaction conditions in the above-mentioned Practical Example and Comparative Examples were as follows:

Φ 38 mm fluidized bed reactor

Reaction temperature	430°C
Reaction pressure	0.14 MPa
Catalyst charge	400 g
Catalyst's propylene load (WWH)	0.085 hr^{-1}
Raw material gas ratio (Moles)	C_3^-/NH$_3$/air = 1/1.2/9.5

[12] 发明专利申请公开说明书

[21] 申请号　00111715.7

[54] 发明名称　丙烯氨氧化生产丙烯腈的流化床催化剂

[57] 摘要

本发明涉及一种丙烯氨氧化生产丙烯腈的流化床催化剂，含有二氧化硅载体和以原子 比计化学式如下的组合物：$A_aB_bC_cGe_dMn_eW_fFe_gBi_hMo_iO_x$ 式中 A 选自 Li、Na、K、Rb 或 Cs 中的至少二种；B 选自 Co、Ni、Cr、Ca、Mg、La、Ce 或 V 中的至少一种；C 选自 B、P 或 As 中的至少一种。本发明催化剂特别适用于在较 低反应温度、较高的反应压力和高丙烯负荷条件下使用，且可保持高的丙烯腈单收和高氨 转化率，可用于工业生产中。

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权 利 要 求 书

1、一种丙烯氨氧化生产丙烯腈的流化床催化剂，含有二氧化硅载体和以原子比计化学式如下的组合物：

$$A_aB_bC_cGe_dMn_eW_fFe_gBi_hMo_iO_x$$

式中 A 选自 Li、Na、K、Rb 或 Cs 中的至少二种；

B 选自 Co、Ni、Cr、Ca、Mg、La、Ce 或 V 中的至少一种；

C 选自 B、P 或 As 中的至少一种；

a 的取值范围为 0.01～1.5；

b 的取值范围为 0.1～12.0；

c 的取值范围为 0.1～0.6；

d 的取值范围为 0.01～2.0；

e 的取值范围为 0.01～2.5；

f 的取值范围为 0.05～1.5；

g 的取值范围为 0.1～4.0；

h 的取值范围为 0.2～2.5；

i 的取值范围为 12.0～14.5；

x 为满足催化剂中各元素化合价所需的氧原子总数；

其中催化剂载体选自二氧化硅，其用量以重量百分比计为 30～70%。

2、根据权利要求 1 所述丙烯氨氧化生产丙烯腈的流化床催化剂，其特征在于 a 的取值范围为 0.01～0.7。

3、根据权利要求 1 所述丙烯氨氧化生产丙烯腈的流化床催化剂，其特征在于 c 的取值范围为 0.1～0.45。

4、根据权利要求 1 所述丙烯氨氧化生产丙烯腈的流化床催化剂，其特征在于 d 的取值范围为 0.01～1.0。

5、根据权利要求 1 所述丙烯氨氧化生产丙烯腈的流化床催化剂，其特征在于 e 的取值范围为 0.2～1.5。

6、根据权利要求 1 所述丙烯氨氧化生产丙烯腈的流化床催化剂，其特征在于 f 的取值范围为 0.1～1.0。

丙烯氨氧化生产丙烯腈的流化床催化剂

本发明涉及丙烯氨氧化生产丙烯腈的流化床催化剂。

丙烯腈是重要的有机化工原料，它是通过丙烯氨氧化反应生产的。为获得高活性、高选择性的流化床催化剂，人们经过不断探索，进行了一系列改进。这些改进大都涉及催化剂活性组成，注重催化剂活性组份之间的搭配，来提高催化剂的活性与选择性，从而达到丙烯腈单程收率的提高，以及生产负荷的提高。

氨氧化法生产丙烯腈经过 30 多年的发展，工厂的生产能力与市场需求已接近平衡。目前丙烯腈生产的主要发展趋势，已由建设新装置转向原有工厂的改造，以进一步降低原料消耗和增加生产能力。通过对原有工厂的改造，更换高效催化剂和消除生产工艺中的瓶颈，丙烯腈的生产能力有可能提高 50～80%，而所需的投资仅为新建装置的 20～30%，经济效益十分巨大。

工厂改造中会产生两个问题：①流化床反应器的反应压力将上升；②催化剂的装载量不能太多。为此要求换用的催化剂应有较高的丙烯负荷和能承受较高的反应压力。

流化床反应器的反应压力是由反应器出口到吸收塔顶之间一系列换热器、塔器和配管的阻力降决定的。由于生产能力的增加使反应器出口的物料量明显增大，使上述阻力降增加。另外，各换热器传热面积不够也需增加换热设备，使阻力降进一步增大。由于环保要求，吸收塔顶的反应废气不准直接排放到大气中，要送到炉子烧掉。这样如果不用引风机，则必须提高吸收塔顶压力。由于上述种种原因，目前反应器的操作压力比设计值要增加 0.5～1.0 倍，即达到 0.08MPa 以上。

上述第二个问题是催化剂的负荷，即 WWH。其定义是每吨催化剂，每小时可以处理的吨数。由于反应器进料量的增加，如果催化剂的负荷不变，则催化剂装载量也要相应增加。但原设计的流化床反应器中冷却水管高度不够，因此反应器中催化剂的流化高度有可能超过冷却水管的高度。另外，由于反应器进料量增大，所以操作线速也显著提高。这两项变化的综合影响有可能使反应器稀相温度上升，造成二氧化碳生成量增大，丙烯腈选择性下降。因此催化剂的 WWH 较高可以防止出现上述问题。另外若能有效降低反应温度，一方面能降低能耗，另一方面也可改善反应状况，达到提高丙烯腈收率的目的。

从理论上来说提高催化剂的 WWH 应当增加催化剂对丙烯的吸附活化能力，但目前尚无催化剂中某种元素可以提高对丙烯吸附活化能力的报导。在文献 CN1021638C 中提出了如下组成的催化剂：

$A_aB_bC_cNi_dCo_eNa_fFe_gBi_hM_iMo_jO_x$

其中 A 为钾、铷、铯、钐、铊；B 为锰、镁、锶、钙、钡、镧、稀土元素；C 为磷、砷、硼、锑、铬；M 为钨、钒。

上述催化剂可以得到较高的丙烯腈单收，但催化剂的丙烯负荷较低，在较高的反应压力下丙烯腈单收下降较大。进一步研究表明，上述催化剂中的组分 B 和 M 对催化剂的负荷和在高压下的性能有关。组分 B 中的某些元素虽然对提高丙烯腈单收有作用，但对催化剂负荷的提高和高反应压力的性能有负面影响，不利于催化剂适应较高压力，较高负荷条件下操作。另外在 CN1021638C 中曾规定上述催化剂组成中，i 和 j 的总和为 12，即是一个常数。在本发明中取消此项规定，因为按此规定 M 组分增加时钼组分将减少，将影响丙烯腈单收。

文献 US5688739 和 US5770757 中介绍了一种获得高丙烯腈收率的含锗氨氧化催化剂。该文献中采用钼、铋、锗体系，任选元素中含碱金属，但实施例中未公开含钠的例子，另外该文献中只公开了反应压力为常压的反应条件，没有在高压、高负荷条件下的具体考察数据。

本发明的目的是要克服上述文献中存在的催化剂未涉及适应较高反应压力、高操作负荷及在反应温度略低条件下反应性能的问题，提供一种新的丙烯氨氧化生产丙烯腈的流化床催化剂。该催化剂能适应在较高的反应压力、较高的负荷及反应温度略低和较低的空气/丙烯比条件下操作，且保持高的丙烯腈单程收率和高氨转化率。

本发明的目的是通过以下的技术方案来实现的：一种丙烯氨氧化流化床催化剂，含有二氧化硅载体和以原子比计化学式如下的组合物：
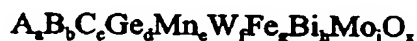
$A_aB_bC_cGe_dMn_eW_fFe_gBi_hMo_iO_x$

式中 A 选自 Li、Na、K、Rb 或 Cs 中的至少二种；

B 选自 Co、Ni、Cr、Ca、Mg、La、Ce 或 V 中的至少一种；

C 选自 B、P 或 As 中的至少一种；

a 的取值范围为 0.01～1.5；

b 的取值范围为 0.1～12.0；

c 的取值范围为 0.1～0.6；

d 的取值范围为 0.01～2.0；

e 的取值范围为 0.01～2.5；

f 的取值范围为 0.05～1.5；

g 的取值范围为 0.1～4.0；

h 的取值范围为 0.2～2.5；

i 的取值范围为 12.0～14.5；

x 为满足催化剂中各元素化合价所需的氧原子总数；

其中催化剂载体选自二氧化硅，其用量以重量百分比计为 30～70%。

上述技术方案中 a 的取值优选范围为 0.01～0.7，c 的取值优选范围为 0.1～0.45，d 的取值优选范围为 0.01～1.0，e 的取值优选范围为 0.2～1.5，f 的取值优选范围为 0.1～1.0。

本发明催化剂的制造方法并无特殊要求，可按常法进行。首先将催化剂各组份制成溶液，再与载体混合制成浆料，经喷雾干燥成型为微球状，最后焙烧制成催化剂。浆料的配制最好按 CN1005248C 方法进行。

制造本发明催化剂的原料为：

催化剂中钼组份用氧化钼或钼酸铵。

催化剂中磷、砷和硼最好用相应的酸类或其铵盐；钨可用钨酸铵或其氧化物；钒可用偏钒酸铵；锗用其氧化物；铬最好用三氧化铬、硝酸铬或二者的混合物；其它组份可用其硝酸盐、氧化物或可分解为氧化物的盐类，但最好用水溶性的硝酸盐。

作为载体二氧化硅的原料可用硅溶胶、硅凝胶或两者的混合物。如果用硅溶胶，其质量要符合 CN1005248C 的要求。

配制好的浆料加热浓缩到固含量为 47～55% 后喷雾干燥。喷雾干燥器可用压力式，两流式或离心转盘式，但以离心式较好，能保证制成的催化剂有良好的粒度分布。

催化剂的焙烧可分为两个阶段进行：催化剂中各元素盐类的分解和高温焙烧。分解阶段温度最好为 200～300℃，时间为 0.5～2 小时。焙烧温度为 500～800℃，最好为 550～700℃；焙烧时间为 20 分钟到 2 小时。上述分解和焙烧在两个焙烧炉内分别进行，也可在一个炉内分为两个区域，也可在连续式旋转焙烧炉内同时完成分解和焙烧。在催化剂分解和焙烧过程中要通入适量空气，防止催化剂被过度还原。

采用本发明催化剂制造丙烯腈所需的丙烯、氨和分子氧的规格与使用其它氨氧化催化剂相同。虽然原料丙烯中的低分子饱和烃含量对反应并无影响，但从经济观点考虑丙烯浓度最好大于 85%(摩尔)。氨可用肥料级液氨。反应所需分子氧从技术角度可用纯氧，富氧

和空气，但从经济和安全考虑最好用空气。

进入流化床反应器的氨与丙烯的摩尔比为 0.8~1.5 之间，最好为 1.0~1.3。空气与丙烯的摩尔比为 8~10.5，最好为 9.0~9.8。如果由于某些操作上的原因须用较高空气比时，可以增大到 11，对反应没有重大影响。但从安全考虑，反应气体中的过量氧不能大于 7%(体积)，最好不大于 4%。

本发明催化剂用于流化床反应器时，反应温度为 420~470℃，最好为 425~450℃。本发明催化剂是一种适用于低反应温度、高压、高负荷催化剂，因此在生产装置中反应压力可在 0.08MPa 以上，例如，0.08~0.15MPa。如果反应压力低于 0.08MPa 也不会有任何不利影响，丙烯腈单收可进一步提高。

本发明催化剂的丙烯负荷(WWH)为 0.06~0.15 小时$^{-1}$，最好为 0.07~0.10 小时$^{-1}$。负荷过低不仅浪费催化剂，也会使二氧化碳生成量增加，选择性下降，是不利的。负荷过高没有实际意义，因为催化剂加入量过少，会使催化剂层内冷却水管的传热面积小于移去反应热所需的面积，造成反应温度无法控制。

用本发明催化剂制造丙烯腈的产品回收精制工艺，可用已有的生产工艺，不需做任何改造。即流化床反应器的流出气体经中和塔除去未反应氨，再用低温水将全部有机产物吸收。吸收液经萃取蒸馏，脱氢氰酸和脱水处理后得高纯度丙烯腈产品。

本发明通过在钼、铋、铁催化体系中加入组份锗和钨，发现该催化体系具有在较高反应压力(0.14MPa)，较高负荷(WWH 为 0.085 小时$^{-1}$)条件下的操作能力，再在催化剂体系中加入组份锰，发现该催化体系在反应温度 430℃条件下，有较高的催化活性与选择性；另外适当添加其他有效活性组份以及非金属元素 B、P 或/和 As，使该催化剂在反应温度 430℃、较高压力 0.14MPa、较高负荷 0.085 小时$^{-1}$和较低空气/丙烯比为 9.5:1(摩尔)条件下操作，其丙烯腈单程收率最高可达 80.3%，且氨转化率可达 98%，取得了较好的效果。

本发明催化剂的活性考评是在内径为 38 毫米的流化床反应器中进行的。催化剂装填量 400 克，反应温度 430℃，反应压力 0.14MPa，原料配比(摩尔)为丙烯：氨：空气＝1：1.2：9.5，催化剂的丙烯负荷(WWH)为 0.085 小时$^{-1}$。

在本发明中丙烯转化率、丙烯腈选择性和单程收率的定义如下：

$$丙烯转化率（\%）= \frac{反应的丙烯摩尔数}{丙烯进料摩尔数} \times 100$$

$$丙烯腈选择性（\%）= \frac{生成丙烯腈摩尔数}{反应的丙烯摩尔数} \times 100$$

$$丙烯腈单程收率（\%）= \frac{生成丙烯腈摩尔数}{丙烯进料摩尔数} \times 100$$

$$氨转化率（\%）= \frac{氨进料摩尔数 - 未反应氨摩尔数}{氨进料摩尔数} \times 100$$

下面通过实施例对本发明作进一步的阐述。

【实施例1】

将2.16克硝酸铯、1.64克硝酸钾混合，加水30克并加热溶解，得到物料(A)；将7.02克二氧化锗、11.48克钨酸铵以及421.8克钼酸铵溶于350克60～90℃热水中，得物料(B)；将10.8克三氧化铬溶于15克水中，得物料(C)；将67.2克硝酸铋、17.47克硝酸锰、282克硝酸镍、48.4克硝酸铈、102克硝酸镁和168克硝酸铁混合，加水190克，加热溶解后作为物料(D)；称取磷酸溶液4.12克作为物料(E)。

将物料(A)与1280克重量浓度为40％的硅溶胶混合，在搅拌下依次加入物料(B)、(C)、(D)和(E)，经充分搅拌后得浆料，依常法将制成的浆料在喷雾干燥器中进行微球粒成型，最后在内径为89毫米，长度为1700毫米(Φ89×1700毫米)的旋转焙烧炉中于590℃焙烧1.5小时，制成组成为

$50\% \ K_{0.1}Cs_{0.07}P_{0.020}Ni_{5.6}Cr_{0.35}Ce_{0.35}Mg_{1.2}Ge_{0.05}Mn_{0.2}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x + 50\%SiO_2$。

【实施例2～8及比较例1～4】

采用与实施例1基本相同的方法制备具有下表中不同组成的催化剂，并用所制得的催化剂在下述反应条件下进行丙烯氨氧化生成丙烯腈的反应，结果见表1。

上述实施例与比较例的反应条件为：

Φ38毫米流化床反应器

反应温度　430℃

反应压力　0.14MPa

催化剂装填量　400克

催化剂丙烯负荷(WWH)　0.085 小时$^{-1}$

原料气配比(摩尔)　$C_3^=$/NH$_3$/空气＝1/1.2/9.5

表 1

实施例	催化剂组成	丙烯腈收率%	丙烯腈选择性%	氨转化率%	丙烯转化率%
实施例 1	$K_{0.1}Cs_{0.07}P_{0.020}Ni_{5.6}Cr_{0.35}Mg_{1.2}Ge_{0.05}Mn_{0.2}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	80.3	81.9	98.0	98.0
实施例 2	$K_{0.1}Cs_{0.07}P_{0.020}Ni_{5.6}Cr_{0.35}Ce_{0.35}Mg_{1.2}Ge_{0.05}Mn_{0.25}W_{0.2}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.9	81.7	97.2	97.8
实施例 3	$K_{0.08}Na_{0.2}Cs_{0.05}P_{0.020}Ni_{5.6}Cr_{0.35}La_{0.30}Mg_{1.2}Ge_{0.05}Mn_{0.2}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.2	81.1	98.1	97.6
实施例 4	$K_{0.08}Na_{0.25}Cs_{0.05}P_{0.020}Ni_{3.0}Cr_{2.5}Ce_{0.33}Mg_{1.2}Ge_{0.05}Mn_{0.2}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.3	81.4	96.9.	97.4
实施例 5	$K_{0.08}Na_{0.2}Cs_{0.2}P_{0.020}Cr_{0.35}Co_{4.5}Ce_{0.33}Ge_{0.1}Mn_{0.25}W_{0.2}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.6	81.0	96.8	98.2
实施例 6	$K_{0.15}Cs_{0.07}P_{0.025}Ni_{3.0}Co_{2.5}Cr_{0.33}Mg_{1.2}Ge_{0.05}Mn_{0.25}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	80.0	81.8	97.4	97.8
实施例 7	$Li_{0.05}Na_{0.2}Rb_{0.065}P_{0.025}Ni_{6.0}Cr_{0.33}La_{0.35}Ge_{0.05}Mn_{0.20}W_{0.15}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	79.0	80.1	98.2	98.6
实施例 8	$K_{0.15}Rb_{0.05}Cs_{0.05}Ni_{3.0}Co_{2.5}Cr_{0.33}Mg_{1.2}Ge_{0.05}Mn_{0.25}W_{0.10}Fe_{2.0}Bi_{0.75}Mo_{13.0}O_x$	78.6	80.7	98.8	97.4
比较例 1	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{3.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.17}Cs_{0.05}O_x$	76.8			
比较例 2	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.4}Co_{4.3}Na_{0.15}W_{0.45}Cr_{0.45}K_{0.45}Cs_{0.07}O_x$	77.1			
比较例 3	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{2.0}Co_{5.0}Na_{0.15}Mn_{0.45}Cr_{0.45}K_{0.21}O_x$	76.2			
比较例 4	$Mo_{12}Bi_{0.9}Fe_{1.8}Ni_{3.0}Mg_{2.0}Na_{0.15}W_{0.45}Cr_{0.45}Cs_{0.09}O_x$	77.4			